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Dissociation of CO_2 by thermal plasma with contracting nozzle quenching

Jiao Li[a], Xiaoqing Zhang[b], Jun Shen[a], Tangchun Ran[a], Pan Chen[a], Yongxiang Yin[a,*]

[a] Centre of Plasma technology, College of Chemical Engineering, Sichuan University, Chengdu, Sichuan, 610065, China
[b] University of Electronics Science and Technology of China, Chengdu, Sichuan, 610060, China

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ABSTRACT

CO_2 decomposition is carried out by a binode thermal plasma reactor with a contracting nozzle quenching. The effects of CO_2/Ar and CO_2/N_2 mixture, CO_2 feed rate, and plasma discharge power on CO_2 conversion and energy efficiency are investigated. The experimental results have turned out the CO_2 conversion increased with the decrease of CO_2 feed rate and increase of discharge power, but energy efficiency shows an opposite tendency. The excellent results of CO_2 conversion 45–48%, energy efficiency 18–19% were achieved by the experimental conditions of N_2/CO_2 = 1, CO_2 flow rate 25 L/min, discharge power 12–15 kW. The results, better than what ever reported, may be contributed to the application of contracting nozzle in combination with a proper cooling tube, which bring about a quick quenching at cooling rate of 10^7 K/s. Moreover, the discharge power, feed flow rate, and the configuration of contracting nozzle must be matched.

1. Introduction

The massive combustion of fossil fuels has resulted in decrease of the fossil fuel reserves and increase of the atmospheric CO_2 concentration, which inevitably leads to the serious energy crisis and ecological problems [1]. Though the renewable energy, such as solar, wind, and nuclear, will become the main energy sources in the future, they are hardly to provide raw hydrocarbon material needed by chemical industry. How to turn electric energy into analogous petrochemical energy effectively is a great strategic issue to meet the demands of rising productivity and modern life style. Therefore, various schemes have been explored. One of these schemes is conversion of water into hydrogen and carbon dioxide into carbon monoxide, then to synthesize hydrocarbons by Fischer-Tropsch process [2,3]. And the key point is to convert CO_2 into CO effectively.

It is well known that CO_2 is a very stable molecule, splitting CO_2 directly to CO is a highly endothermic reaction. Highly conversion rate and energy efficiency of this reaction are usually base on some special methods. Plasma technology (including cold and thermal plasma) is potential to apply in CO_2 decomposition [4–6]. Spencer and Gallimore investigated CO_2 decomposition by radio-frequency plasma operating at 13.56 MHz with CO_2/Ar mixtures [7]. The maximum energy efficiency obtained was only 3% when CO_2 conversion was 20% at the power of 250 W, CO_2 feed flow of 100 sccm; the maximum CO_2 conversion was 90% but energy efficiency was 0.3% at 1000 W, CO_2 feed flow of 15 sccm. Tsuji et al. [8] carried out decomposition of CO_2 in a microwave (2.45 GHz) discharge plasma with CO_2/He or CO_2/Ar mixtures. They found that the decomposition of CO_2 in CO_2/Ar was higher than that in CO_2/He, the maximum energy efficiency of 4.6% and CO_2 conversion was 90% at power of 100 W, CO_2 feed flow of 25 sccm. Mei et al. [9] did CO_2 splitting by dielectric barrier discharge plasma with packing of $BaTiO_3$. They pointed out that CO_2 decomposition and energy efficiency were promoted by dielectric materials, the maximum energy efficiency of 7.0% was obtained when CO_2 conversion was 13.5% at power of 20 W, CO_2 feed flow of 50 sccm. Indarto et al. [10] conducted CO_2 decomposition by AC gliding arc plasma. The maximum energy efficiency of 20% was obtained when CO_2 conversion was 15% at power of 230 W, CO_2 feed flow of 1.40 L/min.

Compared to cold plasmas mentioned above, which decompose CO_2 by energetic electron impact at gas temperature less than 1000 K [11,12], CO_2 splitting by thermal plasma is a pyrolysis process at temperature of more than 3500 K, the key problem is how to prevent the reverse reaction when the pyrolysis gas goes out of the reactor. Yun et al. [13] carried out decomposition of carbon dioxide by thermal plasma with a water-cooled tube quenching. The conversion of CO_2 reported was less than 11%, and the energy efficiency was not higher than 0.48%. Huczko and Szymafiski [14] investigated CO_2 pyrolysis by Ar plasma with a plate heat exchanger. The CO_2 conversion and energy efficiency were 7% and 5.2%, respectively. They did a mechanism and kinetic analysis and pointed out that a quenching rate of more than 10^7 K/s would be very important to determine the final conversion efficiency of CO_2.

In this paper, thermal plasma is employed to decompose CO_2. In order to suppress the inverse reaction of CO_2 splitting, a quenching

* Corresponding author.
E-mail address: hyyx0675@sina.com (Y. Yin).

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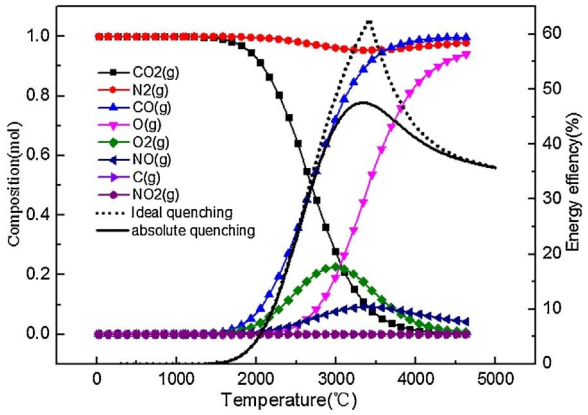

Fig. 1. Thermodynamic equilibrium and theoretical energy efficiency of CO_2 thermal cracking at atmospheric pressure.

method of supersonic contracting nozzle combined with proper water-cooled tube is adopted.

2. Thermodynamic analysis

The CO_2 decomposition in thermal plasma can be considered as pyrolysis, When there is some nitrogen in the reaction system, the main reactions in this process are as follows:

$$CO_2 \rightarrow CO + \frac{1}{2}O_2 \quad (1)$$

$$N_2 + 2CO_2 \rightarrow 2NO + 2CO \quad (2)$$

$$CO_2 \rightarrow C(g) + O_2 \quad (3)$$

$$O_2 \rightarrow O + O \quad (4)$$

$$NO + O \rightarrow NO_2 \quad (5)$$

Fig. 1 shows the thermodynamic equilibrium calculation of CO_2 pyrolysis in different temperature at atmospheric pressure. It can be seen that, as a strong endothermic reaction, CO_2 thermal dissociation begins at temperature of 1800 ˚C, the conversion can reach 75% with selectivity of CO almost 100% at temperature of 3000 ˚C. Nitrogen addition impact on CO_2 conversion is very small.

Obviously, for CO_2 pyrolysis reaction, high temperature is favorable for forming CO, O and O_2. However, a quick quenching of 10^7 K/s is necessary. Theoretically, there are two specific quenching modes: absolute quenching and ideal quenching [15].

For absolute quenching, the target products are saved but some unstable atoms and radicals are combined themself into stable molecule. For example, CO is saved but O atoms are combined into O_2 in the present case.

For ideal quenching, not only the target products are saved but the unstable atoms or radicals will further react into target products. For example, some O atoms will further react with CO_2 and convert into CO and O_2. That is why ideal quenching usually result in higher conversion than that by absolute quenching. According to theoretical energy efficiency calculation of CO_2 pyrolysis, which are shown in Fig. 1. The highest energy efficiency reached are 47.5% and 62.7% by absolute quenching and ideal quenching, respectively.

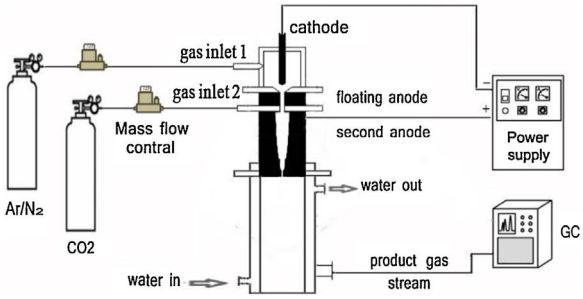

Fig. 2. schematic view of the experimental setup.

3. Experiment

3.1. Experimental setup

The schematic view of the experimental setup for CO_2 dissociation by thermal plasma is shown in Fig. 2. The DC thermal plasma generator (or reactor) is composed of one cathode and two columnar anodes. They are fixed separately and coaxially by insulating materials. There are two gas inlets on the reactor, one is located between the cathode and the first anode (or floating anode), the other is located between the floating anode and the second anode (or working anode).

Argon or nitrogen, and CO_2 are introduced into reactor from inlet 1 and inlet 2, respectively. The floating anode acts as a trigger, when a defined high voltage is applied between floating anode and cathode, there is a breakdown through the gas which is blow to the second anode. The second anode is supplied with a DC voltage. By the conductivity of ionized gas a stable arc is set up and maintained between cathode and the second anodes. The gas fed into the reactor then is instantaneously heated to thousands Kelvin by arc, and CO_2 is cracked at the same time. To quench the pyrolysis gas, a contracting nozzle with the throat diameter in millimeters is installed at the exit of second anode, which lead the pyrolysis gas jetting into a water-cooled tube with diameter of 200 mm. The produced gas is sampled at the exit of the cooling tube, and analysed by gas chromatography.

3.2. Analysis method

The gas products are mainly consisted of CO_2, CO, O_2 and Ar or N_2. The volume fractions of these gases are analysed by a two-channel gas chromatograph equipped with a thermal conductivity detector (TCD) and a backflush system (SC-200G-05T, Chuanyi), as shown in Fig. 3. The front channel contains a TDX-01 column and a Molecular sieve 5A column in series. During measurements, the sample gas is fed into the first column (TDX-01), where CO_2 is separated from other gases (CO, O_2 and Ar or N_2), and then connected to the TCD detector. As the second column (Molecular sieve 5A column) will be contaminated by CO_2, the back-flush system is switched on after CO, O_2 and Ar or N_2 have entered first column. By this way, CO_2 belatedly goes into TCD, then vents; the mixture of CO, O_2 and Ar or N_2 go into Molecular sieve 5A column for separation, then go into TCD again.

As there is not solid carbon found in our experiments, the carbon conservation in gas phase before and after reaction is assumed. Some relationships are established,

$$V^*_{tot} = V_{CO2}/(F_{CO} + F_{CO2}) \quad (6)$$

$$V^*_{CO2} = F_{CO2} \times V^*_{tot} \quad (7)$$

Where, V_{CO2} (L/min) denote the volume flow rate CO_2 in the feed gas, F_{CO2} (%), F_{CO} (%) are the volume fractions of CO_2 and CO from GC in sample gas, respectively. V_{tot}^* and V_{CO2}^* (L/min) denote the volume flow rate of gas mixture and CO_2 after reaction, respectively. Finally, CO_2 conversion is calculated by